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THERMAL FEATURES, THERMOLYSIS AND THERMOCHEMISTRY OF HEXACHLOROSTANNATES OF SOME MONONITROGEN AROMATIC BASES

TADEUSZ JANIAK and JERZY BŁAŻEJOWSKI

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

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ABSTRACT

Thermal properties of the hexachlorostannates of several nitrogen aromatic bases (B) have been examined applying thermoanalytical methods. All the compounds studied undergo decomposition upon heating, leading to their total volatilization, according to the equation

$$(BH)_2SnCl_6(crys.) \longrightarrow 2B(g) + 2HCl(g) + SnCl_4(g)$$

The enthalpies of the above process have been evaluated from the non-isothermal thermogravimetric curves using the van't Hoff equation. These values, together with the thermochemical characteristics available in the literature, were used to evaluate the enthalpies of formation and the crystal lattice energies of the compounds. The latter quantity was also examined on the basis of the Kapustinskii–Yatsimirskii formula. Thermoanalytical data indicate the existence of two stages in the volatilization process which have different kinetics. The kinetic phenomena have been analysed using the Jacobs and Russell-Jones theory for the dissociative volatilization process and a standard approach based on the Arrhenius model. The influence of the structure of organic bases on the thermal behaviour of their hexachlorostannates is also discussed.

INTRODUCTION

Mononitrogen aromatic bases (i.e. pyridine, quinoline, acridine and their homologues and derivatives) (B) interact in condensed phases with Lewis or Brönsted acids, forming adducts or salt-type derivatives. Particularly interesting are compounds belonging to the latter group that contain typical inorganic anions and BH^+ cations. Numerous properties of such derivatives are typical for ionic compounds, e.g. solubility in polar media, dissociation into ions in molten state and solutions, formation of ionic crystal lattices, etc. On the other hand, these compounds possess many features characteristic of the original bases, e.g. spectral properties. Such compounds are thus convenient model systems for studying the behaviour of derivatives that are on the boundary between typical inorganic and organic derivatives. Since nitrogen organic bases occur commonly in biological systems as such or as a

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part of macromolecules, the knowledge of their properties is important for understanding the role they play in biochemistry. The salt-type derivatives of nitrogen organic bases are also widely used as catalysts of numerous processes, among others those realized on an industrial scale. Thus, a knowledge of properties of these compounds is of considerable practical importance.

This work is a part of a general research program concerning the investigations of the thermal behaviour and thermochemistry of salt-type derivatives of nitrogen organic bases. In several earlier works we have demonstrated that thermoanalytical methods are a very useful tool in examination of the thermal features of hydrochlorides of alkanamines [1], aromatic monoamines [2] and mononitrogen aromatic bases [3]. To have a further insight into the nature and properties of salt-type derivatives of nitrogen organic bases, it is necessary to extend the phenomenological basis to examining compounds containing more complex anions. The negative ions should be stable so that during thermal decomposition they will preserve their identity. We chose the symmetrical, octahedral $SnCl_6^{2-}$ ion, which is distinguished from other hexachlorometallate ions by relatively high thermal stability [4]. The latter feature of $SnCl_6^{2-}$ results from the relatively low Sn^{4+}/Sn^{2+} redox potential ($+0.15$ V [5]) compared with that of $Cl_2/2Cl^-$ ($+1.36$ V [6]). Thus, the central atom does not show any tendency to reduction by the surrounding chloride ions. This was fully confirmed by studies of the thermal dissociation of hexachlorostannates of alkanamines [7].

The chemistry of the compounds chosen for examination in this work has not been studied extensively in the past. The hexachlorostannates of simple representatives of mononitrogen aromatic bases have been known for a long time [8–13]; however, only some of their spectral [14–16] and structural [16–19] features have so far been examined. There is actually only a little known on the thermochemistry and thermal properties of these derivatives [9–12,16,20] or related compounds [21,22], which prompts a need for undertaking studies in the latter area. By conducting such investigations we expected to gather more information on the nature of interactions between acids and nitrogen organic bases. Further, such studies should provide added information on the behaviour of highly unsymmetrical ions. Lastly, the studies should give further insight into the thermodynamics and kinetics of dissociative volatilization processes.

EXPERIMENTAL

All reagents were the best available grades and were purified, when necessary, by standard methods. The hexachlorostannates were prepared by mixing the aqueous solutions of hydrochlorides of nitrogen bases with

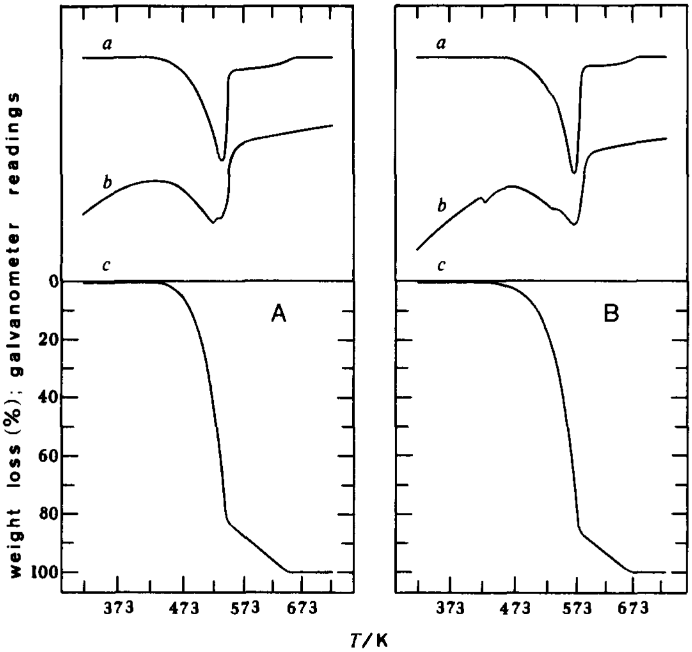


Fig. 1. Thermal analyses of pyridinium hexachlorostannate (A) and 3,4-dimethylpyridinium hexachlorostannate (B) performed in dynamic mode. *a*, Differential thermogravimetry; *b*, differential thermal analysis; *c*, thermogravimetry.

stoichiometric amounts of a solution of $SnCl_4 \cdot 5H_2O$ in dilute HCl (molar ratio 2 : 1) [7,11,16]. The crystals formed were filtered off, carefully washed with 0.1 M HCl solution, and dried in a vacuum desiccator over NaOH and P_2O_5. The compositions of the compounds were confirmed by elemental analysis (performed on a Carlo-Erba model 1106 instrument).

TABLE 1

Values of α and T for the first step of volatilization of pyridinium (A), 3,4-dimethylpyridinium (B) and quinolinium (C) hexachlorostannates

α	T (K)		
	A	B	C
0.08	478.3	507.7	488.3
0.16	494.7	526.7	502.3
0.24	504.3	538.3	511.0
0.32	512.7	548.3	517.3
0.40	518.7	553.0	522.3
0.48	523.7	561.0	526.7
0.56	529.0	566.0	530.3
0.64	534.0	570.7	533.7
0.72	538.7	574.7	537.3
0.80	–	578.7	–

The dynamic thermal analyses were carried out on an OD-103 derivatograph (Monicon), with α-Al_2O_3 as reference, in a dynamic nitrogen atmosphere. The samples, weighing 100 mg, were placed on one platinum plate of the multi-plate sample holder (see ref. 23, Appendix 1, No. 4). All analyses were carried out at a heating rate of 4.85 ± 0.05 K min^{-1}.

Thermogravimetric (TG) analysis under quasi isothermal–isobaric conditions was performed on a Q-1500 derivatograph (Monicon) by placing a sample weighing 90 mg in a special platinum labyrinth crucible (for details of the method see ref. 24). The sample was heated with a rate of ca. 3 K min^{-1}. The rate of mass loss was adjusted to be 2 mg min^{-1}.

From the TG curves, such as those shown in Fig. 1, values of the temperature T corresponding to certain values of the extent of reaction α can be derived [25]. For each compound examined a set of α vs. T data points was determined on the basis of at least three replicate measurements. An example is given in Table 1.

RESULTS AND DISCUSSION

Thermal behaviour of the hexachlorostannates

The results of a typical thermoanalytical measurement are shown in Fig. 1. To enable further discussion of the thermal properties of the compounds studied, characteristic parameters resulting from the examination of the thermal analysis curves are compiled in Table 2 together with available literature information.

All the compounds studied undergo complete volatilization on heating up to 650 K. The TG curves demonstrate that the process proceeds essentially in two stages. The first step, in which up to 86% of the sample is volatilized, is followed by a slow process, seen as a 'tail', in which the remaining part of the sample disappears. A similar effect has been observed on thermal dissociation of alkanaminium chlorides [1] and hexachlorostannates [7], as well as hydrochlorides of aromatic amines [2] and mononitrogen aromatic bases [3]. It has been demonstrated, by complementary examination, that a residue which volatilizes in the second stage has the same composition as the original sample. It is thus probable that the observed effect is a consequence of a diminution of the rate of the process as a result of some physical processes occurring in a volatilized material. We will discuss this issue subsequently.

The smooth shape of the TG curves corresponding to the first step of the volatilization is somewhat disturbed in the case of 3,5-dimethylpyridinium and isoquinolinium hexachlorostannates. The two above mentioned compounds undergo transformations at temperatures of 486 K and 503 K, respectively (Table 2), accompanied by relatively strong endothermic effects

TABLE 2

Thermal characteristics of hexachlorostannates of nitrogen aromatic bases

No.	Substance	Peak temperature [a] (K)				T [a] (K)			Parameters describing the onset of the second stage	
		DTG	DTA			$T_{0.08}$	$T_{0.72}$	ΔT		
			T_p	T_σ	T_m				α	T (K)
1	Pyridine	534	534	331 [16]; 520 [b]	578 [11]; 572–579(d) [c]	478.3	538.7	60.4	0.78	540
2	3-Methylpyridine	525	528	–	453 [b]; 445–455 [c]	471.0	526.7	55.7	0.80	530
3	4-Methylpyridine	536	536	472 [b]	503–518(d) [c]; 527 [b]	482.0	536.3	54.3	0.79	540
4	2,4-Dimethylpyridine	544	542	487 [b]	503–512(d) [c]; 514 [b]	487.0	542.0	55.0	0.83	550
5	3,4-Dimethylpyridine	568	569	431 [b]; 541 [b]	555–563(d) [c]	507.7	574.7	67.0	0.84	585
6	3,5-Dimethylpyridine	484 562	558	486 [b]	502–509(d) [c]	–	–	–	0.86	570
7	2,4,6-Trimethylpyridine	549	546	–	551–557(d) [c]	497.0	549.3	52.3	0.80	555
8	Quinoline	537	539	–	531–532 [11]; 524–533(d) [c]; 539 [10]	488.3	537.3	49.0	0.84	545
9	2-Methylquinoline	541	540	–	–	497.3	549.0	51.7	0.75	550
10	Isoquinoline	503 567	567	503 [b]	538 [12]; 543–565(d) [c]	–	–	–	0.85	575
11	Acridine	569	567	–	593–609(d) [c]	514.3	572.3	58.0	0.77	575

[a] The symbols were taken from ref. 26. T_p, Temperature of the peak; T_σ, temperature of the solid state phase transition; T_m, temperature of melting; T_α, temperature at which the fraction reacted is equal to α; ΔT, $T_{0.72} - T_{0.08}$.

[b] T_m or T_σ determined from DTA curves.

[c] T_m determined by the standard capillary method; (d) indicates melting with decomposition.

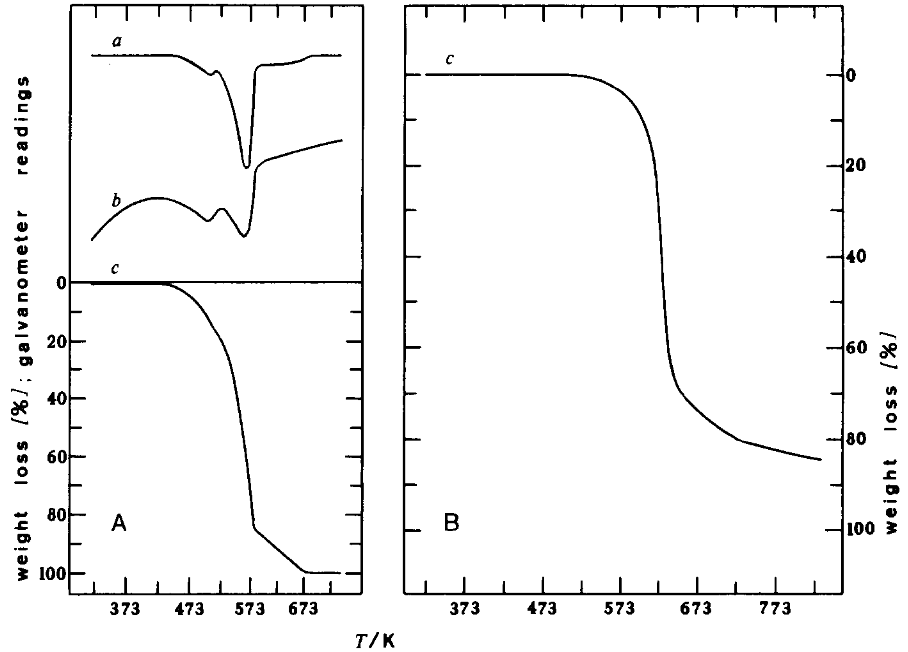


Fig. 2. Thermal analyses of isoquinolinium hexachlorostannate carried out in dynamic mode (A) and Q-mode (B). *a*, Differential thermogravimetry; *b*, differential thermal analysis; *c*, thermogravimetry.

and slight loss of mass. These processes are seen as weak, poorly resolved peaks in differential thermogravimetric (DTG) curves and side inflections in TG curves (see, e.g., Fig. 2A). To have further insight into the nature of these effects, we performed analyses of both compounds in Q-mode. Generally, this method allows better separation of processed not resolved in standard dynamic measurements. Surprisingly, the effects discussed, seen, e.g., in Fig. 2A, are not observed in the Q-TG curves of either compound (cf., e.g., Fig. 2B). This means that these processes are of physical nature. We therefore ascribed them to solid state phase transitions, since the melting point values reported in the literature and those determined by the capillary method, in the case of both compounds, fall in the much higher temperature region. It is, however, not clear why the solid phase transition is accompanied by a slight loss in mass of the sample. The possible explanation is that the volatilization process starts from the low temperature phase and is abated upon transformation to the high temperature phase.

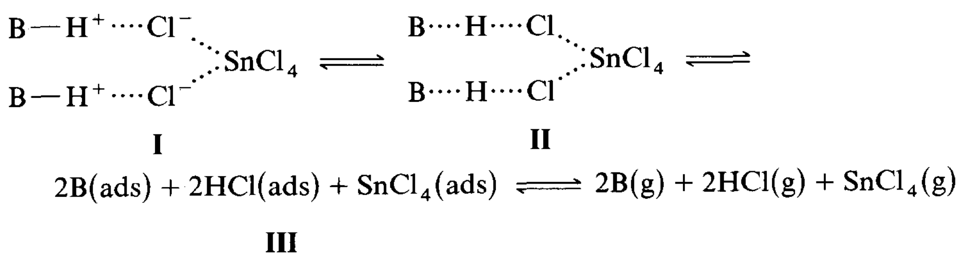
Thorough examination of the thermal analysis curves and the discussion above reveal that volatilization of several compounds studied (i.e. pyridinium, 4-methylpyridinium, 2,4-dimethylpyridinium, 3,4-dimethylpyridinium and isoquinolinium hexachlorostannates) is preceded by solid state phase transitions and some of them (e.g. that of 3-methylpyridinium hexachlorostannate) by fusion. In the case of 3-methylpyridinium hexachlorostannate, the peak in the DTA curve at 453 K was ascribed to melting because of the closeness of this value and the melting point value determined by the capillary method. However, the endothermal effect accompanying this process is extremely strong and could well arise also from polymorphic transition occurring simultaneously with fusion. It is worth noting that extremely strong endothermic effects also accompany phase transition in 4-methylpyridinium hexachlorostannate, and, as mentioned above, 3,5-dimethylpyridinium and isoquinolinium hexachlorostannates. A comparison of the literature melting points, and those determined either from DTA or standard capillary measurements, with values of the peak temperatures corresponding to the dissociation process (T_p values in DTA and DTG), as well as values of $T_{0.08}$ and $T_{0.72}$, reveals that the majority of the compounds decompose while melting. The effects originating from fusion are seen only in DTA curves of three of the compounds studied. This is because melting points correspond to temperatures at which the volatilization process is far advanced and, presumably, the relatively weak thermal effects resulting from fusion are masked by much stronger effects originating from the volatilization process. An exception is 2-methylquinolinium hexachlorostannate. The volatilization of this compound is not preceded by any phase change.

Peak temperatures in DTG and DTA, as well as $T_{0.08}$ and $T_{0.72}$ values, gradually increase with an increase in the size of the cation of a given aromatic base. However, this tendency is less pronounced than in the case of the boiling points of the corresponding bases [6,27]. On the other hand, temperature limits for the volatilization of hexachlorostannates (ΔT) do not show any dependence on the size of the cation.

It may perhaps be worth mentioning that volatilization of hexachlorostannate salts of mononitrogen aromatic bases begins at temperatures that are several tens of K higher than those characterizing the onset of decomposition of the corresponding chloride salts.

Nature of the volatilization process

Owing to the quite strong basic character of the nitrogen aromatic bases, their complex compounds containing protonated forms of the parent molecules show, in condensed phases, many features of typical ionic substances (see, e.g., ref. 3 and references cited therein). This fact led us to believe that hexachlorostannates of nitrogen bases behave similarly to other salts of nitrogen bases. This implies also that the mechanism of the volatilization of the compounds studied should exhibit the same features as the mechanism, discussed by us previously, of thermolysis of alkanaminium hexachlorostannates [4,7] and chlorides [1], as well as other chloride salts of nitrogen bases [2,3]. To rationalize the problem, the scheme of volatilization is presented below, which shows possible stages for the process



$$\left.\begin{matrix} B{-}H^{+}\cdots Cl^{-} \\ B{-}H^{+}\cdots Cl^{-} \end{matrix}\right\}\!\cdots SnCl_4 \rightleftharpoons \left.\begin{matrix} B\cdots H\cdots Cl \\ B\cdots H\cdots Cl \end{matrix}\right\}\!\cdots SnCl_4 \rightleftharpoons$$

$$\text{I} \qquad\qquad \text{II}$$

$$\underset{\text{III}}{2B(ads) + 2HCl(ads) + SnCl_4(ads)} \rightleftharpoons 2B(g) + 2HCl(g) + SnCl_4(g) \tag{1}$$

This scheme involves three steps in the thermal dissociation process, namely: (i) proton transfer in the ion triplet at the position of a half-crystal site (**I**), which creates the transition state (**II**); (ii) dissociation of the molecule in the transition state followed by the formation of a mobile adsorbed phase (**III**), and (iii) desorption of adsorbed molecules from the surface. The migration of the molecules over the surface of the condensed phase followed by their diffusion through the gas phase represents the volatilization process.

There was much controversy regarding the mechanism of the volatilization of simple salts of nitrogen bases, namely hydrohalides of ammonia, in the early decades of this century. It has finally been established that these derivatives undergo complete dissociation into NH_3 and HX upon volatilization [28–30]. However, several recent theoretical calculations [31–34] and certain experimental evidence [34–37] indicate that simple alkanamines and HX (X = Cl, Br, I) are to some extent associated in the gaseous phase. The energy of these interactions can be of the order of a few tens of kJ per mol. It is difficult to predict how far the molecules transferred to the gaseous phase upon volatilization of the compounds studied interact with one another. In view of the above discussion such a possibility really exists, taking into account that both HCl and $SnCl_4$ exhibit features of Lewis acids. Also, weak interaction between base molecules cannot be excluded [38]. The energy of all the above mentioned interactions is rather small in comparison with the enthalpy change accompanying the volatilization process. Therefore, it seems justifiable to assume that all the evolved fragments behave as kinetically free molecules in the gaseous phase.

Enthalpy of volatilization

The extent of the thermal dissociation α at a given temperature T determines directly the partial pressure of gaseous components. Therefore the enthalpy of volatilization ΔH_v can be evaluated on the basis of the van't Hoff equation if the system, at any moment, attains thermal equilibrium. This is achieved when the only barrier existing for the process is a thermo-

TABLE 3

Thermochemical and kinetic constants for the volatilization of hexachlorostannates of nitrogen aromatic bases

Substance (no. from Table 2)	From eqn. (2) [a]		From eqn. (3) [b]			
	ΔH_v (kJ mol^{-1})	T_v (K)	$g(1-\alpha)=\alpha$ (R1)		$g(1-\alpha)$ $=1-(1-\alpha)^{1/2}$ (R2)	
			E (kJ mol^{-1})	Z (s^{-1})	E (kJ mol^{-1})	Z (s^{-1})
1	394	546	372	1.9×10^3	415	7.9×10^3
2	416	534	394	7.9×10^3	440	3.9×10^4
3	448	544	426	2.2×10^4	474	1.2×10^5
4	433	552	410	8.7×10^3	465	6.1×10^4
5	396	586	373	6.2×10^2	422	3.0×10^3
7	480	557	457	5.5×10^4	509	3.4×10^5
8	493	545	472	1.6×10^5	525	1.1×10^6
9	489	556	466	8.5×10^4	520	5.5×10^5
11	463	582	441	1.1×10^4	490	5.6×10^4

[a] The values of ΔH_v and T_v were evaluated using a standard least-squares procedure. The correlation coefficient was always better than 0.999.

[b] Equation (3) was rearranged to the form $\ln[g(1-\alpha)/T]$ vs. $1/T$ and values of E and Z were evaluated by a least-squares procedure. The correlation coefficient was always better than 0.998 in the case of the R1 model and better than 0.999 for the R2 model.

chemical one, i.e. ΔH_v. Under these conditions the experimental degree of conversion is equal to P/P_0, where P is the equilibrium vapor pressure at a given temperature and P_0 is the atmospheric pressure. ΔH_v can be then derived from the equation

$$\ln \alpha = -\frac{\Delta H_v}{5R}\frac{1}{T} + \frac{\Delta H_v}{5R}\frac{1}{T_v} \tag{2}$$

where R is the gas constant, the factor of 5 accounts for the fact that the dissociation of 1 mol of $(BH)_2SnCl_6$ yields 5 mol of gaseous products and T_v represents the volatilization temperature, i.e. the temperature at which P attains P_0. To realize the process possibly close to the equilibrium conditions, the analyses were carried out at a moderate heating rate and using as small a sample as possible. Furthermore, the compounds were analysed in thin layers placed on a relatively large surface to enable free diffusion of gaseous products and to avoid side processes.

Using experimental α vs. T dependences the values of ΔH_v were evaluated, and these are listed in Table 3. In the case of 3,5-dimethylpyridinium and isoquinolinium hexachlorostannates the above procedure could not be applied, since the compounds do not volatilize in one well defined stage. Reviewing the data in Table 3, one notices an increase of ΔH_v with both the number of aromatic rings and the number of alkyl substituents in the molecule. An increase of T_v values with an increase of the molecular mass of the base may also be observed.

Kinetics of the thermal dissociation

The volatilization of hexachlorostannates of nitrogen aromatic bases cannot be considered as a simple physical process since it involves a chemical reaction. This category of processes is named dissociative volatilization processes to distinguish them from chemical reactions on one side and from typical processes on the other. The kinetics of such processes may be examined by the application of a standard approach based on the Arrhenius concept. The use of this method under dynamic conditions has been discussed elsewhere [39,40].

Following this approach, the general integral equation describing kinetics of solid phase reactions can be derived, namely this given

$$g(1-\alpha) = Z\frac{T}{\phi}\exp[-E/(5RT)] \qquad (3)$$

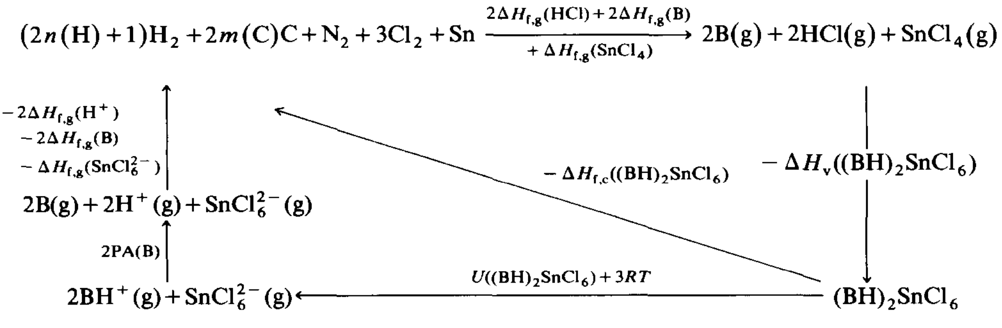
where $g(1-\alpha)$ represents the kinetic model for the process, ϕ is the heating rate and Z and E are Arrhenius constants (E identifies the activation barrier for the process). The exponential term in eqn. (3) includes the factor 5. This modification of the classical Arrhenius equation is a result of the examination of kinetics of volatilization of chloride and hexachlorostannate salts of alkanamines and other nitrogen bases [1–4,7]. It implies that the transition state for the dissociative volatilization of the hexachlorostannates studied is a loosely bound complex of two molecules of HCl, two molecules of nitrogen base and an $SnCl_4$ molecule. Following the suggestion of Meshi and Searcy [41], the Arrhenius equation should then be considered against 5 molecules of gaseous products released from the simplest structural unit of the hexachlorostannate molecule.

Using the experimental α vs. T dependences and eqn. (3), the values of Z and E were derived and these are listed in Table 3. In these calculations we have considered two reaction models, namely, the zero kinetic order model (R1) and the contracting surface area model (R2) [25]. We chose these models since they seem to be the most adequate for our experimental conditions. Moreover, the R2 model has been proposed in the past for description of the kinetics of volatilization of some ammonium salts [42,43]. The examination of the kinetic constants shown in Table 3 reveals that E values characterizing the R1 model are always somewhat lower than ΔH_v values, whereas activation barriers corresponding to the R2 model are always slightly higher than the relevant ΔH_v values. Both models fit equally well the experimental data points. If, indeed, this simple approach described the kinetic phenomena accompanying dissociative volatilization of the compounds studied, the determined activation energies would indicate that the process does not actually require to overcome the additional energy barrier over that resulting from the enthalpy change for the reaction, i.e. ΔH_v. This conclusion strengthens the earlier assumption on the close-to-equilibrium course of the process. It should be remembered, however, that this method presents only a purely formal approach to the kinetic phenomena without true insight into the microscopic mechanism of the volatilization.

The Arrhenius model fits very well the experimental thermogravimetric curves in the first step of volatilization. The question remains, however, as how to explain the existence of the second stage in the process, seen as a 'tail' in TG curves. Thorough examination of the problem reveals that this effect must be caused by kinetic phenomena. Semi-quantitative explanation of the effect is possible on the basis of Jacobs and Russell-Jones theory for the dissociative volatilization processes [42]. We have discussed this issue in several earlier studies (see, e.g., refs. 1–4 and 7). To our knowledge the effect of diminution of the rate of the process occurs when the dimensions of drops or crystals become relatively small. This is a result of an increase of cohesive forces. However, such an effect should influence the volatilization process gradually and should affect thermogravimetric curves smoothly. It is thus probable that at the point characterizing the beginning of the second stage some non-continuous processes take place. One such process could be cracking of a thin layer of the liquid substance covering the whole surface of a flat platinum crucible, and formation of small drops from which the volatilization process is restricted. Most of the compounds studied melt before or during volatilization and to these derivatives the above explanation can be applied. However, a similar effect is observed if a solid substance undergoes exclusively sublimation, e.g. 2-methylquinolinium hexachlorostannate. It is thus clear that the nature of this phenomenon is much more complex and further studies are necessary for its better understanding.

Thermochemical characteristics

Many thermochemical quantities for the compounds studied can be derived from the simple Hess' law. The various relations between the thermochemical quantities are presented in Scheme 1 in the form of a



Scheme 1.

thermochemical cycle. All magnitudes in the cycle refer to 298 K and 1 atmosphere. ΔH_f denotes the enthalpy of formation of a given substance; $U+3RT$ is the lattice enthalpy; U represents the lattice energy; PA denotes the proton affinity of the base; ΔH_v identifies the enthalpy of volatilization; $n(\mathrm{H})$ and $m(\mathrm{C})$ represent the number of hydrogen and carbon atoms, respectively, in the simplest unit of the salt molecule.

From Scheme 1 the following relationships result

$$\Delta H^\ominus_{f,c}[(\mathrm{BH})_2\mathrm{SnCl}_6] = 2\Delta H^\ominus_{f,g}(\mathrm{HCl}) + 2\Delta H^\ominus_{f,g}(\mathrm{B}) + \Delta H^\ominus_{f,g}(\mathrm{SnCl}_4) - \Delta H^\ominus_v[(\mathrm{BH})_2\mathrm{SnCl}_6] \tag{4}$$

$$\Delta H^\ominus_{f,g}(\mathrm{BH}^+) = \Delta H^\ominus_{f,g}(\mathrm{B}) + \Delta H^\ominus_{f,g}(\mathrm{H}^+) - PA(\mathrm{B}) \tag{5}$$

$$U^\ominus[(\mathrm{BH})_2\mathrm{SnCl}_6] = 2\Delta H^\ominus_{f,g}(\mathrm{BH}^+) + \Delta H^\ominus_{f,g}(\mathrm{SnCl}_6^{2-}) - \Delta H^\ominus_{f,c}[(\mathrm{BH})_2\mathrm{SnCl}_6] - 3RT \tag{6}$$

The ΔH_v values determined using eqn. (2) do not refer to 298 K. Therefore they have to be modified according to the equation

$$\Delta H^\ominus_{v,298} = \Delta H_v + \Delta H^\ominus_{fn} + \Sigma\Delta H^\ominus_\sigma - \int_{298}^{T} \Delta C_p^\ominus \mathrm{d}T \tag{7}$$

where $\Delta H^\ominus_{fn}$ is the enthalpy of fusion; the term $\Sigma\Delta H^\ominus_\sigma$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of the fusion or volatilization process, while $\int_{298}^{T}\Delta C_p^\ominus \mathrm{d}T$ accounts for the change in enthalpy resulting from changes in the heat capacities of the reactants. The enthalpy of fusion of 3-methylpyridinium hexachlorostannate was estimated to be 28 kJ mol^{-1}. This value has been obtained by comparison of the area of DTA peak at 453 K with that resulting from the volatilization process and assuming that the latter area corresponds to the ΔH_v value listed in Table 3. For the remaining compounds the term $\Delta H^\ominus_{fn}$ was neglected, since the compounds melt and decompose simultaneously ($T_m > T_{0.08}$). It is thus difficult to assess how far the process of fusion affects the thermodynamics of volatilization of these derivatives. Analogously to the above, the enthalpies of phase transitions in 4-methylpyridinium and 3,4-dimethylpyridinium hexachlorostannates (at 431 K) were evaluated to be 44 and 9 kJ mol^{-1}, respectively. Furthermore, it was assumed that phase transitions in 2,4-dimethylpyridinium and 3,4-dimethylpyridinium hexachlorostannates (at 541 K) do not influence the thermodynamics of the volatilization process, since $T_\sigma > T_{0.08}$. The magnitude of the heat capacity term is difficult to estimate in the absence of heat capacity data for hexachlorostannates and their decomposition fragments. In our earlier work we demonstrated that the heat capacity term for sublimation of $(\mathrm{NH}_4)_2\mathrm{SnCl}_6$ is ca. -10 kJ mol^{-1} [4]. This value was assumed arbitrarily in this work for the heat capacity term in eqn. (7). At least two facts justify such an assumption. First, volatilization of alkanaminium hexachlorostan-

TABLE 4

Thermochemical characteristics for mononitrogen aromatic bases, their cations and hexachlorostannates at 298 K

Substance, B	B		BH^+		$(BH)_2SnCl_6$			
	$\Delta H^{\ominus}_{f,g}$ (kJ mol^{-1})	*PA* (kJ mol^{-1})	$\Delta H^{\ominus}_{f,g}$ (kJ mol^{-1})	r_C (nm)	$\Delta H^{\ominus}_{v}$ (kJ mol^{-1})	$\Delta H^{\ominus}_{f,c}$ (kJ mol^{-1})	$U^{\ominus}$ (kJ mol^{-1})	
							From the thermochemical cycle	From eqn. (8)
Pyridine	140.4 [a]	930 [d]	747	0.203 [e]	404	−780	1111	1246
3-Methylpyridine	106.4 [a]	944 [d]	699	0.229 [e]	454	−898	1133	1197
4-Methylpyridine	104.1 [a]	948 [d]	692	0.220 [e]	502	−950	1171	1214
2,4-Dimethylpyridine	63.9 [a]	957 [d]	643	0.215 [e]	443	−972	1095	1223
3,4-Dimethylpyridine	70.1 [a]	952 [d]	654	0.206 [e]	415	−931	1076	1240
3,5-Dimethylpyridine	72.8 [a]	949 [d]	660	0.207 [e]	–	–	–	1238
2,4,6-Trimethylpyridine	44.7 [b]	972 [e]	609	0.218 [e]	490	−1057	1112	1217
Quinoline	216.7 [c]	954 [d]	799	0.201 [e]	503	−726	1161	1249
2-Methylquinoline	176	969	743	0.203 [f]	499	−804	1127	1246
Isoquinoline	201.7 [c]	951 [d]	787	0.202 [e]	–	–	–	1248
Acridine	292.5 [c]	976 [d]	853	0.197 [e]	473	−545	1088	1257

[a] ref. 44. [b] ref. 45. [c] ref. 46. [d] ref. 48. [e] ref. 3. [f] Value estimated by combining $\Delta H^{\ominus}_{f,g}$ and *PA* for 2-methylquinoline given in this table with thermochemical data for the hydrochloride of the base taken from our previous work [3].

nates proceeds over a temperature range similar to that for the sublimation of $(NH_4)_2SnCl_6$. Secondly, the expected changes in heat capacity brought about by an increase in the size of the alkyl group should be identical for salts and for the corresponding bases. The corrected values of $\Delta H_v^\ominus$ are listed in Table 4.

The values of the enthalpy of formation of most of the nitrogen bases have been taken from the literature (cf. Table 4). The enthalpy of formation of gaseous 2-methylquinoline was estimated on the basis of Benson's group additivity scheme [47], by deriving values of appropriate group parameters by comparison of the heats of formation of pyridine, methyl-substituted pyridines and quinoline [44]. Proton affinities listed in Table 4 were also taken from the literature and were corrected relative to the proton affinity of NH_3, 860 kJ mol^{-1} [49]. For the proton affinity of 2-methylquinoline a value equal to 969 kJ mol^{-1} was assumed by analysing *PA* data in Table 4 and Ref. 48. Using values of $\Delta H_{f,g}^\ominus(B)$ and $PA(B)$ (Table 4) together with the values of $\Delta H_v^\ominus$ evaluated in this work (Table 4), and taking $\Delta H_{f,g}^\ominus(H^+) = 1536.2$ kJ mol^{-1} [50], $\Delta H_{f,g}^\ominus(HCl) = -92.3$ kJ mol^{-1} [50], $\Delta H_{f,g}^\ominus(SnCl_4) = -472$ kJ mol^{-1} [50], and $\Delta H_{f,g}^\ominus(SnCl_6^{2-}) = -1156$ kJ mol^{-1} [51], we derived values of the enthalpies of formation of crystalline hexachlorostannates and crystal lattice energies of the compounds, which are listed in Table 4. The heats of formation of gaseous BH^+ ions are also listed in Table 4.

To facilitate further discussion regarding the crystal lattice energy problem, we invoked an approximate method developed originally by Kapustinskii and Yatsimirskii [52,53]. According to these authors the crystal lattice energy of ionic compounds can be expressed with the equation

$$U\ (\text{in kJ mol}^{-1}) = 120.2\frac{(\Sigma n)\ Z_C Z_A}{r_C + r_A}\left[1 - \frac{0.0345}{r_C + r_A} + 0.087(r_C + r_A)\right] \qquad (8)$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule, Z_C and Z_A denote the numerical values of the charges of cation and anion, respectively, and r_C and r_A are the 'thermochemical' ionic radii (in nm). Using values of r_C from our previous work [3] (Table 4) and assuming for $r_{SnCl_6^{2-}}$ a value of 0.37 nm [7], we derived values of U which are shown in the last column of Table 4.

CONCLUSIONS

Four compounds studied, namely 3-methylpyridinium, 4-methylpyridinium, 3,5-dimethylpyridinium and isoquinolinium hexachlorostannates, undergo solid state phase transitions which are accompanied by extremely strong endothermal effects. The entropy changes for transitions in 3-methylpyridinium and 4-methylpyridinium hexachlorostannates are equal to 62 and 93 J mol^{-1} K^{-1}, respectively. These values are much higher than the entropy change accompanying phase transition in 3,4-dimethylpyridinium hexachlorostannate at 431 K, equal to 21 J mol^{-1} K^{-1}. The entropy of phase transitions in alkanaminium chlorides amount usually to several J mol^{-1} K^{-1} [1,54]. The same concerns phase transition in methanaminium hexachlorostannate [55]. These facts indicate that reorganization of the crystal lattice, towards a disordered phase, of the four above mentioned compounds must be well advanced. We did not observe such an effect previously [1–4,7].

The experimental methods applied in this work appeared to be very useful in examination of the thermal properties and thermochemistry of the compounds studied. Particularly important is the evaluation of basic thermochemical characteristics for the compounds, which so far have not been available. Several assumptions on, among others, the equilibrium character of the volatilization process and ideal behaviour of gaseous products imply that the derived thermochemical quantities cannot be accepted entirely without reservation. In several earlier papers, regarding thermal decomposition and thermochemistry of various salts of nitrogen bases [1–4,7], we have however demonstrated that the derived characteristics, i.e. enthalpies of formation and crystal lattice energies, compare well with those determined by other methods. Furthermore, the observed discrepancies fall within the uncertainties accompanying determination of other, similar quantities, e.g. proton affinities or heats of formation of bases. The most probable source of discrepancies seems to be the disregard of interactions of the decomposition products in the gaseous phase. The magnitude of these interactions could be evaluated by the application of semi-empirical quantum chemistry methods, e.g. MNDO. We attempt to examine this problem.

The enthalpies of formation of hexachlorostannate salts of mononitrogen aromatic bases are lower than those of alkanaminium hexachlorostannates [7], but are much higher than the enthalpies of formation of hydrochlorides of these bases [3]. This indicates that hexachlorostannates are more stable than hydrochlorides. Indeed, the compounds studied begin to decompose at temperatures exceeding, by up to 100 K, those characterizing volatilization of the corresponding hydrochlorides [3]. Furthermore, hexachlorostannates do not show a tendency to form hydrates, solvates or compounds containing more molecules of $SnCl_4$ or HCl than results from the $(BH)_2SnCl_6$ stoichiometry, unlike hydrochlorides of aromatic bases [3].

Despite the obvious increase in the size of the cation over the series pyridine (py), quinoline and acridine, on the one hand, and their methyl substituted derivatives on the other hand, the differences between U values are insignificant. The values of crystal lattice energy for the compounds studied are comparable to values of U for alkanaminium hexachlorostannates containing small substituents or only partially substituted on the aminium ions [1]. These comparisons indicate that crystal lattice energy is not influenced by the actual size of the cation. In attempting to find an explanation for this fact let us recall the meaning of the crystal lattice energy. This quantity accounts for the energy difference resulting from the transfer of kinetically free ions from the gaseous phase to the crystal lattice. In ionic lattices, which we believe are formed by the compounds studied, the crystal lattice energy is determined predominantly by electrostatic interactions, i.e. the position and magnitude of charged centres. Numerous crystallographic studies on alkanaminium chlorides [56–58], hydrochlorides of aromatic amines [59], and nitrogen aromatic bases [60] revealed that the linear hydrogen bond $N-H \cdots Cl$, whose distance is affected only insignificantly by the substitution at nitrogen, plays an important role in the structure of these salts. Since the charged centres in the latter derivatives are most probably located on nitrogen and chlorine atoms, similar values for the crystal lattice energies can be expected. This was fully confirmed experimentally [1–3]. The lattices of hexachlorostannate salts of nitrogen bases are composed of structural units consisting of octahedral $SnCl_6^{2-}$ ions connected with base cations by a polyfurcated hydrogen bond of the type $N-H \cdots Cl-M$ [16,18,19,61,62]. In these derivatives $SnCl_6^{2-}$ octahedra form the skeleton of the lattice and base cations fill the free space in the interior [16,18]. The crystallographic data for $(PyH)_2SnCl_6$ demonstrate that each pyridinium cation is actually connected via a trifurcated hydrogen bond to two neighbouring $SnCl_6^{2-}$ octahedra [16]. This hydrogen bond involves two Cl atoms from one $SnCl_6^{2-}$ octahedron and one Cl atom from a neighbouring $SnCl_6^{2-}$ ion. A second pyridinium cation bonds two of the three Cl atoms participating in the above described trifurcated bond. This way four Cl atoms of each $SnCl_6^{2-}$ octahedron are involved in bonding two base cations. In the lattice described the main force keeping molecules in the crystal is coulombic interaction. The electrostatic interactions depend on the charge distribution and position of charged centres in the lattice, i.e. mainly the position of Cl and N atoms. Both the above characteristics are unaffected by the size and structure of the cation. Thus, the coulombic part of the lattice energy should be similar for all the compounds studied, and this is fully confirmed by the results of our studies. The differences in the crystal lattice energies of the individual derivatives can be partially accounted for by the van der Waals interactions between base cation rings. Crystallographic data for $(PyH)_2SnCl_6$ show that pyridinium rings are situated in nearly parallel planes relatively close to each other [16].

The formation of crystal lattices of hexachlorostannates of aromatic bases seems to be more favourable than formation of lattices of the corresponding chloride salts. This results from the fact that the $SnCl_6^{2-}$ ion corresponds better to base cations than does Cl^- ion with regard to both size and structure [16]. This explains qualitatively the observed relatively high stability of hexachlorostannate salts.

The values of U calculated using the Kapustinskii–Yatsimirskii equation are roughly 100 kJ mol^{-1} higher than those evaluated from the thermodynamic cycle (Table 4). In the calculations we used values of r_C which had been derived from the known crystal lattice energies of the corresponding chloride salts. The disagreement between crystal lattice energy values obtained by the two methods clearly demonstrates that the Kapustinskii–Yatsimirskii approach does not apply to salts of highly unsymmetrical ions. For such ions 'thermochemical' radii are not additive quantities. Non-applicability of this approach presumably results from the above discussed differences in the nature of the hydrogen bonds formed.

Further insight into crystal lattice problems could be made by calculating the crystal lattice interactions on the basis of knowledge of the crystal structure. We are currently working on this problem.

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